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(54) **High foaming nonionic surfactant based liquid detergent.**

(57) A high foaming, light duty liquid detergent with desirable cleansing properties and mildness to the human skin comprising : a water soluble nonionic surfactant ; a water soluble or dispersible foaming, anionic surfactant ; a zwitterionic betaine surfactant.

EP 0 633 308 A1

Background Of The Invention

The present invention relates to novel light duty liquid detergent compositions with high foaming properties, containing a nonionic surfactant, a specific group of anionic surfactants, and a Zwitterionic betaine surfactant wherein the surfactants are dissolved in an aqueous medium.

Nonionic surfactants are in general chemically inert and stable toward pH change and are therefore well suited for mixing and formulation with other materials. The superior performance of nonionic surfactants on the removal of oily soil is well recognized. Nonionic surfactants are also known to be mild to human skin. However, as a class, nonionic surfactants are known to be low or moderate foamers. Consequently, for detergents which require copious and stable foam, the application of nonionic surfactants is limited. There have been substantial interest and efforts to develop a high foaming detergent with nonionic surfactants as the major ingredient. Little has been achieved.

The prior art is replete with light duty liquid detergent compositions containing nonionic surfactants in combination with anionic and/or betaine surfactants wherein the nonionic detergent is not the major active surfactant, as shown in U.S. Patent No. 3,658,985 wherein an anionic based shampoo contains a minor amount of a fatty acid alkanolamide. U.S. Patent No. 3,769,398 discloses a betaine-based shampoo containing minor amounts of nonionic surfactants. This patent states that the low foaming properties of nonionic detergents renders its use in shampoo compositions non-preferred. U.S. Patent No. 4,329,335 also discloses a shampoo containing a betaine surfactant as the major ingredient and minor amounts of a nonionic surfactant and of a fatty acid mono- or di-ethanolamide. U.S. Patent No. 4,259,204 discloses a shampoo comprising 0.8-20% by weight of an anionic phosphoric acid ester and one additional surfactant which may be either anionic, amphoteric, or nonionic. U.S. Patent No. 4,329,334 discloses an anionic-amphoteric based shampoo containing a major amount of anionic surfactant and lesser amounts of a betaine and nonionic surfactants.

U.S. Patent No. 3,935,129 discloses a liquid cleaning composition based on the alkali metal silicate content and containing five basic ingredients, namely, urea, glycerin, triethanolamine, an anionic detergent and a nonionic detergent. The silicate content determines the amount of anionic and/or nonionic detergent in the liquid cleaning composition. However, the foaming property of these detergent compositions is not discussed therein.

U.S. Patent No. 4,129,515 discloses a heavy duty liquid detergent for laundering fabrics comprising a mixture of substantially equal amounts of anionic and nonionic surfactants, alkanolamines and magnesium salts, and, optionally, zwitterionic surfactants as suds modifiers.

U.S. Patent No. 4,224,195 discloses an aqueous detergent composition for laundering socks or stockings comprising a specific group of nonionic detergents, namely, an ethylene oxide of a secondary alcohol, a specific group of anionic detergents, namely, a sulfuric ester salt of an ethylene oxide adduct of a secondary alcohol, and an amphoteric surfactant which may be a betaine, wherein either the anionic or nonionic surfactant may be the major ingredient.

The prior art also discloses detergent compositions containing all nonionic surfactants as shown in U.S. Patent Nos. 4,154,706 and 4,329,336 wherein the shampoo compositions contain a plurality of particular nonionic surfactants in order to effect desirable foaming and detergative properties despite the fact that nonionic surfactants are usually deficient in such properties.

U.S. Patent No. 4,013,787 discloses a piperazine based polymer in conditioning and shampoo compositions which may contain all nonionic surfactant or all anionic surfactant.

U.S. Patent No. 4,450,091 discloses high viscosity shampoo compositions containing a blend of an amphoteric betaine surfactant, a polyoxybutylenepolyoxyethylene nonionic detergent, an anionic surfactant, a fatty acid alkanolamide and a polyoxyalkylene glycol fatty ester.

U.S. Patent No. 4,595,526 describes a composition comprising a nonionic surfactant, a betaine surfactant, an anionic surfactant and a C₁₂-C₁₄ fatty acid monoethanolamide foam stabilizer.

However, none of the above-cited patents discloses a high foaming, nonionic based, liquid detergent composition containing a nonionic surfactant, a supplementary high foaming ethoxylated alkyl ether sulfate anionic surfactant and a supplementary foaming zwitterionic surfactant selected from betaine type surfactants as the three essential ingredients wherein the composition does not contain any amine oxide, calcium carbonate, polymeric or clay thickeners, abrasive, clays, silicas, alkyl glycine surfactant, cyclic imidinium surfactant, or more than 3.0 wt. % of a fatty acid or a metal salt of the fatty acid compounds.

None of the above-cited patents discloses a high foaming, nonionic based, liquid detergent composition containing a nonionic surfactant as a major active ingredient and lesser amounts of a magnesium salt of C₈-C₁₈ ethoxylated alkyl ether sulfate surfactant, an alkali metal salt of an alkyl sulfate surfactant, and a supplementary foaming zwitterionic surfactant selected from betaine type surfactants as the four essential ingredients, wherein the nonionic ingredient constitutes more than 50% of the total surfactant content.

Summary Of The Invention

It has now been found that a high foaming liquid detergent can be formulated with a nonionic surfactant which has desirable cleaning properties, mildness to the human skin.

5 An object of this invention is to provide novel, liquid aqueous detergent compositions containing a nonionic surfactant, an ethoxylated alkyl (ether) sulfate anionic surfactant, and a zwitterionic betaine surfactant, wherein the composition does not contain amine oxide, alkali metal carbonate, polymeric or clay thickeners, clays, abrasives, alkyl glycine surfactants, cyclic imidinium surfactants, silicas or more than 3 wt. % of a fatty acid or a metal salt of a fatty acid.

10 A further object of this invention is to provide novel, nonionic based, liquid detergent compositions containing a major amount of nonionic surfactant supplemented with lesser amounts of a magnesium salt of an ethoxylated alkyl ether sulfate surfactant, a sodium salt of an alkyl sulfate surfactant, and a zwitterionic betaine surfactant, wherein the composition does not contain any amine oxide, fatty acid alkanolamides, clay, silica, abrasive, clay or polymeric thickeners, alkali metal or alkaline earth metal carbonate or more than 3 wt. % of a fatty acid or its metal salt.

15 Still another object of this invention is to provide a novel, liquid detergent with desirable high foaming and cleaning properties which is mild to the human skin.

Additional objects, advantages and novel features of the invention will be set forth in part in the description which follows, and in part will become apparent to those skilled in the art upon examination of the following or may be learned by practice of the invention. The objects and advantages of the invention may be realized and attained by means of the instrumentalities and combinations particularly pointed out in the appended claims.

20 To achieve the foregoing and other objects and in accordance with the purpose of the present invention, as embodied and broadly described herein the novel, high foaming, light duty liquid detergent of this invention comprises three essential surfactants: a water soluble, ethoxylated, nonionic surfactant; a foaming water soluble, zwitterionic surfactant selected from the class of betaines; and an ethoxylated alkyl ether sulfate surfactant, wherein the ingredients are dissolved in an aqueous vehicle, and the composition does not contain any amine oxide, alkanolamide ingredients.

25 More specifically, the present invention relates to a high foaming, nonionic based, liquid detergent comprising a nonionic surfactant selected from the group consisting of water soluble primary aliphatic alcohol ethoxylates, secondary aliphatic alcohol ethoxylates, alkyl phenol ethoxylates and alcohol ethylene oxide propylene oxide condensates; a water soluble zwitterionic betaine surfactant; ethoxylated alkyl ether sulfate surfactants; and optionally a C₈₋₁₄ alkyl sulfate surfactant wherein the ingredients are dissolved in an aqueous vehicle.

30 The total amount of surfactants may constitute 18 %-55 %, preferably 20 % - 40 %, most preferably 25 % - 35 %, by weight of the liquid composition.

Detailed Description Of The Invention

35 The invention relates to a high foaming, nonionic surfactant-based, light duty, liquid detergent comprising approximately, by weight :

(a) 10 % to 25 % of a water soluble nonionic surfactant selected from the group consisting of primary and secondary C₈-C₁₈ alkanol condensates with 5 to 30 moles of ethylene oxide, condensates of C₈-C₁₈ alkyl-phenol with 5 to 30 moles of ethylene oxide, condensates of C₈-C₂₀ alkanol with a heteric mixture of ethylene oxide and propylene oxide having a weight ratio of ethylene oxide to propylene oxide from 2.5:1 to 4:1 and a total alkylene oxide content of 60% to 85% by weight and condensates of 2 to 30 moles of ethylene oxide with sorbitan mono and tri- C₁₀-C₂₀ alkanolic acid esters having an HLB of 8 to 15;

(b) 2 % to 12 % of a water-soluble betaine; and

(c) 8 to 16 % of an ethoxylated alkyl ester sulfate; and

(d) balance being water as an aqueous medium in which said nonionic surfactant, said ethoxylated alkyl ether sulfate and said betaine are solubilized in said water.

40 A preferred composition is a liquid detergent composition further including 1.0 to 15 % of a cosolubilizing agent selected from the group consisting of C₂-C₃ mono- and di-hydroxy alkanols, water soluble salts of C₁-C₃ alkyl substituted benzene sulfonate hydrotropes and mixtures thereof.

45 The high foaming nonionic based light duty liquid detergent compositions of the instant invention comprise approximately by weight : 10 to 25 wt. % of a water soluble nonionic surfactant; 8 to 16 wt. % of an ethoxylated alkyl ether sulfate and 2 to 12 wt. % of a betaine surfactant; and 47 to 80 wt. % of water, wherein the compositions do not contain any amine oxides, calcium carbonate, polymeric or clay thickeners, abrasives, clays, sil-

icas, alkyl glycine surfactants, cyclic imidinium surfactants, or more than 3 wt. % of a fatty acid or a metal salt of the fatty acid.

The invention also relates to a high foaming, nonionic surfactant-based, light duty, liquid detergent comprising approximately, by weight :

- (a) 10 % to 20% of a water soluble nonionic surfactant selected from the group consisting of primary and secondary C₈-C₁₈ alkanol condensates with 5 to 30 moles of ethylene oxide, condensates of C₈-C₁₈ alkylphenol with about 5 to 30 moles of ethylene oxide, condensates of C₈-C₂₀ alkanol with a heteric mixture of ethylene oxide and propylene oxide having a weight ratio of ethylene oxide to propylene oxide from about 2.5:1 to 4:1 and a total alkylene oxide content of 60 % to 85 % by weight and condensates of about 2 to 30 moles of ethylene oxide with sorbitan mono and tri- C₁₀-C₂₀ alkanolic acid esters having an HLB of 8 to 15;
- (b) 8 to 16 % of a magnesium salt of a ethoxylated (C₈-C₁₈) alkyl ether sulfate surfactant;
- (c) 0.5 to 8 % of an alkali metal or ammonium salt of C₈-C₁₄ alkyl sulfate surfactant;
- (d) 2 to 10 % of a water-soluble betaine surfactant; and
- (e) balance being water as an aqueous medium in which said surfactants are solubilized in said water.

Said composition comprises approximately by weight : 10 to 20 wt. %, more preferably 11 to 17 wt. % of a nonionic surfactant; 0.5 to 8 wt. % more preferably 1 to 7 wt. % of an alkali metal or ammonium salt of a C₈-C₁₄ alkyl sulfate surfactant; 8 to 16 wt. % of a magnesium salt of a C₈-C₁₈ ethoxylated alkyl ether sulfate surfactant and 2 to 10 wt. %, more preferably 3 to 9 wt. % of a betaine zwitterionic surfactant, wherein the composition does not contain any amine oxide, fatty acid alkanolamide, alkali metal or alkaline earth metal carbonate, clay, silica, abrasive, clay or polymeric thickener or more than 3 wt. % of fatty acid or its metal salt.

A preferred composition is a liquid detergent composition which includes, in addition, 1% to 15% by weight of a solubilizing agent which is a C₂-C₃ mono or dihydroxy alkanol or a water soluble salts of C₁-C₃ alkyl substituted benzene sulfonate hydrotropes and mixtures thereof.

The nonionic surfactant which constitutes the major ingredient in the liquid detergent composition is present in amounts of 10 to 25 %, preferably 15 to 20 % by weight of the composition and provides superior performance in the removal of oily soil and mildness to human skin.

The water soluble nonionic surfactants utilized in this invention are commercially well known and include the primary aliphatic alcohol ethoxylates, secondary aliphatic alcohol ethoxylates, alkylphenol ethoxylates and ethylene-oxidepropylene oxide condensates on primary alkanols, such as Plurafacs (BASF) and condensates of ethylene oxide with sorbitan fatty acid esters such as the Tweens (ICI). The nonionic synthetic organic detergents generally are the condensation products of an organic aliphatic or alkyl aromatic hydrophobic compound and hydrophilic ethylene oxide groups. Practically any hydrophobic compound having a carboxy, hydroxy, amido, or amino group with a free hydrogen attached to the nitrogen can be condensed with ethylene oxide or with the polyhydration product thereof, polyethylene glycol, to form a water soluble nonionic detergent. Further, the length of the polyethenoxy hydrophobic and hydrophilic elements.

The nonionic detergent class includes the condensation products of a higher alcohol (e.g., an alkanol containing 8 to 18 carbon atoms in a straight or branched chain configuration) condensed with 5 to 30 moles of ethylene oxide, for example, lauryl or myristyl alcohol condensed with 16 moles of ethylene oxide (EO), tridecanol condensed with 6 moles of EO, myristyl alcohol condensed with 10 moles of EO per mole of myristyl alcohol, the condensation product of EO with a cut of coconut fatty alcohol containing a mixture of fatty alcohols with alkyl chains varying from 10 to 14 carbon atoms in length and wherein the condensate contains either 6 moles of EO per mole of total alcohol or 9 moles of EO per mole of alcohol and tallow alcohol ethoxylates containing 6 EO to 11 EO per mole of alcohol.

A preferred group of the foregoing nonionic surfactants are the Neodol ethoxylates (Shell Co.), which are higher aliphatic, primary alcohol containing 9-15 carbon atoms, such as C₉-C₁₁ alkanol condensed with 8 moles of ethylene oxide (Neodol 91-8), C₁₂₋₁₃ alkanol condensed with 6.5 moles ethylene oxide (Neodol 23-6.5), C₁₂₋₁₅ alkanol condensed with 12 moles ethylene oxide (Neodol 25-12), C₁₄₋₁₅ alkanol condensed with 13 moles ethylene oxide (Neodol 45-13), and the like. Such ethoxamers have an HLB (hydrophobic lipophilic balance) value of 8 to 15 and give good O/W emulsification, whereas ethoxamers with HLB values below 8 contain less than 5 ethyleneoxide groups and tend to be poor emulsifiers and poor detergents.

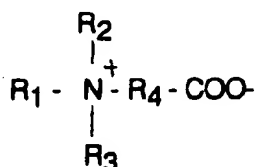
Additional satisfactory water soluble alcohol ethylene oxide condensates are the condensation products of a secondary aliphatic alcohol containing 8 to 18 carbon atoms in a straight or branched chain configuration condensed with 5 to 30 moles of ethylene oxide. Examples of commercially available nonionic detergents of the foregoing type are C₁₁-C₁₅ secondary alkanol condensed with either 9 EO (Tergitol 15-S-9) or 12 EO (Tergitol 15-S-12) marketed by Union Carbide.

Other suitable nonionic detergents include the polyethylene oxide condensates of one mole of alkyl phenol

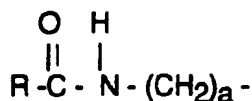
containing from 8 to 18 carbon atoms in a straight- or branched chain alkyl group with 5 to 30 moles of ethylene oxide. Specific examples of alkyl phenol ethoxylates include nonyl phenol condensed with 9.5 moles of EO per mole of nonyl phenol, dinonyl phenol condensed with 12 moles of EO per mole of dinonyl phenol, dinonyl phenol condensed with 15 moles of EO per mole of phenol and diisooctylphenol condensed with 15 moles of EO per mole of phenol. Commercially available nonionic surfactants of this type include Igepal CO-630 (nonyl phenol ethoxylate) marketed by GAF Corporation.

Condensates of 2 to 30 moles of ethylene oxide with sorbitan mono- and tri-C₁₀-C₂₀ alkanolic acid esters having a HLB of 8 to 15 also may be employed as the nonionic detergent ingredient in the described shampoo. These surfactants are well known and are available from Imperial Chemical Industries under the Tween trade name. Suitable surfactants include polyoxyethylene (4) sorbitan monolaurate, polyoxyethylene (4) sorbitan monostearate, polyoxyethylene (20) sorbitan trioleate and polyoxyethylene (20) sorbitan tristearate.

The water-soluble zwitterionic surfactant, which is also an essential ingredient of present liquid detergent composition, constitutes 2 to 12%, preferably 3 to 10%, by weight and provides good foaming properties and mildness to the present liquid detergent. The zwitterionic surfactant is a water soluble betaine having the general formula:



wherein R₁ is an alkyl group having 10 to 20 carbon atoms, preferably 12 to 16 carbon atoms, or the amido radical:



wherein R is an alkyl group having 9 to 19 carbon atoms and a is the integer 1 to 4; R₂ and R₃ are each alkyl groups having 1 to 3 carbons and preferably 1 carbon; R₄ is an alkylene or hydroxyalkylene group having from 1 to 4 carbon atoms and, optionally, one hydroxyl group. Typical alkyldimethyl betaines include decyl dimethyl betaine or 2-(N-decyl-N, N-dimethyl-ammonia) acetate, coco dimethyl betaine or 2-(N-coco N, N-dimethylammonio) acetate, myristyl dimethyl betaine, palmityl dimethyl betaine, lauryl dimethyl betaine, cetyl dimethyl betaine, stearyl dimethyl betaine, etc. The amidobetaines similarly include cocoamidoethylbetaine, cocoamidopropyl betaine and the like. A preferred betaine is coco (C₈-C₁₈) amidopropyldimethyl betaine.

The anionic sulfate and sulfonate surfactants which may be used in the detergent of this invention are water soluble such as triethanolamine and include the sodium, potassium, ammonium and ethanolammonium salts of C₈-C₁₄ alkyl sulfates such as lauryl sulfate, myristyl sulfate and the like; linear C₈-C₁₈ alkyl benzene sulfonates; preferably C₉-C₁₆ or C₁₀-C₁₅.

The preferred sulfate surfactant is a C₈ to C₁₄ alkyl sulfate and is present in the composition at a concentration of about 0.5 to 8 wt. %. A preferred alkylbenzene sulfonate is a linear alkylbenzene sulfonate having a higher content of 3-phenyl (or higher) isomers and a correspondingly lower content (well below 50%) of 2-phenyl (or lower) isomers, such as those sulfonates wherein the benzene ring is attached mostly at the 3 or higher (for example 4, 5, 6 or 7) position of the alkyl group and the content of the isomers in which the benzene ring is attached in the 2 or 1 position is correspondingly low. Preferred materials are set forth in U.S. Patent 3,320,174, especially those in which the alkyls are of 10 to 13 carbon atoms.

The ethoxylated alkyl ether sulfate (AEOS.xEO) is depicted by the formula: R-(OCH₂CH₂)_xOSO₃M wherein x is about 1 to 22, more preferably about 1 to about 10 and R is an alkyl group having about 8 to 18 carbon atoms and more preferably about 12 to about 15 carbon atoms and natural cuts for example C₁₂₋₁₄, C₁₂-C₁₃ and C₁₂₋₁₅ and M is an alkali earth metal cation such as magnesium. Examples of satisfactory anionic ethoxylated sulfate are the ethoxylated C₈₋₁₈ alkyl ether sulfate salts having the formula: R'(OCH₂-CH₂)_nOSO₃M wherein R' is alkyl of 8 or 9 to 18 carbon atoms, n is 1 to 22, preferably 1 to 5, and M is a magnesium cation. The ethoxylated alkyl ether sulfates may be made by sulfating the condensation product of ethylene oxide and

C₈₋₁₈ alkanol, and neutralizing the resultant product. The ethoxylated alkyl ether sulfates differ from one another in the number of carbon atoms in the alcohols and in the number of moles of ethylene oxide reacted with one mole of such alcohol. Preferred ethoxylated alkyl ether sulfates contain 10 to 6 carbon atoms in the alcohols and in the alkyl groups thereof.

5 The particular combination of Na(AEOS.XEO) surfactant, anionic surfactant, and betaine surfactant, provides a detergent system which coacts with the nonionic surfactant to product a liquid detergent composition with desirable foaming, foam stability and deterative properties. Surprisingly, the resultant homogeneous liquid detergent exhibits the same or better foam performance, both as to initial foam volume and stability of foam in the presence of soils, and cleaning efficacy as an anionic based light duty liquid detergent (LDLD) as shown

10 in the following Examples.

The essential ingredients discussed above are solubilized in an aqueous medium comprising water and optionally, solubilizing ingredients such as alcohols and dihydroxy alcohols such as C2-C3 mono- and di-hydroxy alkanols, e.g. ethanol, isopropanol and propylene glycol. Suitable water soluble hydrotropic salts include sodium, potassium, ammonium and mono-, di- and triethanolammonium salts of (C₁-C₃) alkyl substituted benzene sulfonate hydrotropes. While the aqueous medium is primarily water, preferably said solubilizing agents are included in order to control the viscosity of the liquid composition and to control low temperature cloud clear properties. Usually, it is desirable to maintain clarity to a temperature in the range of 5°C to 10°C. Therefore, the proportion of solubilizer generally will be from 0.5% to 8%, preferably 1% to 7%, by weight of the detergent composition with the proportion of ethanol, when present, being 5% of weight or less in order to

20 provide a composition having a flash point above 46° C. Preferably the solubilizing ingredient will be propylene glycol. Another extremely effective solubilizing or cosolubilizing agent used at a concentration of 0.1 to 5 wt. percent, more preferably 0.5 to 4.0 weight percent is isethionic acid or an alkali metal salt of isethionic acid having the formula

25



wherein X is hydrogen or an alkali metal cation, preferably sodium.

30 The foregoing solubilizing ingredients also facilitate the manufacture of the inventive compositions because they tend to inhibit gel formation.

In addition to the previously mentioned essential and optional constituents of the light duty liquid detergent, one may also employ normal and conventional adjuvants, provided they do not adversely affect the properties of the detergent. Thus, there may be used various coloring agents and perfumes; ultraviolet light absorbers such as the Uvinuls, which are products of GAF Corporation; sequestering agents such as ethylene diamine tetraacetates; magnesium sulfate heptahydrate; pearlescing agents and opacifiers; pH modifiers; etc. The proportion of such adjuvant materials, in total will normally not exceed 15% of weight of the detergent composition, and the percentages of most of such individual components will be 0.1% to 5% by weight and preferably less than 2% by weight. Sodium formate can be included in the formula as a preservative at a concentration of 0.1 to 4.0%. Sodium bisulfite can be used as a color stabilizer at a concentration of 0.01 to 0.2 wt.%. Typical preservatives are dibromodicyano-butane, citric acid, benzylic alcohol and poly (hexamethylene-biguamide) hydrochloride and mixtures thereof.

The instant compositions can contain 0 to 5 wt. %, more preferably 1 to 4.0 wt. % of an alkyl polysaccharide surfactant. The alkyl polysaccharides surfactants, which are used in conjunction with the aforementioned surfactant have a hydrophobic group containing from 8 to 20 carbon atoms, preferably from 10 to 16 carbon atoms, most preferably from 12 to 14 carbon atoms; and polysaccharide hydrophilic group containing from 1.5 to 10, preferably from 1.5 to 4, most preferably from 1.6 to 2.7 saccharide units (e.g., galactoside, glucoside, fructoside, glucosyl, fructosyl; and/or galactosyl units). Mixtures of saccharide moieties may be used in the alkyl polysaccharide surfactants. The number x indicates the number of saccharide units in a particular alkyl polysaccharide surfactant. For a particular alkyl polysaccharide molecule x can only assume integral values. In any physical sample of alkyl polysaccharide surfactants there will be in general molecules having different x values. The physical sample can be characterized by the average value of x and this average value can assume non-integral values. In this specification the values of x are to be understood to be average values. The hydrophobic group (R) can be attached at the 2-, 3-, or 4- positions rather than at the 1-position, (thus giving e.g. a glucosyl or galactosyl as opposed to a glucoside or galactoside). However, attachment through the 1- position, i.e., glucosides, galactoside, fructosides, etc., is preferred. In the preferred product the additional saccharide units are predominately attached to the previous saccharide unit's 2-position. Attachment through the 3-, 4-, and 6-

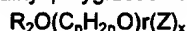
positions can also occur. Optionally and less desirably there can be a polyalkoxide chain joining the hydrophobic moiety (R) and the polysaccharide chain. The preferred alkoxide moiety is ethoxide.

Typical hydrophobic groups include alkyl groups, either saturated or unsaturated, branched or unbranched containing from 8 to 20, preferably from 10 to 18 carbon atoms. Preferably, the alkyl group is a straight chain saturated alkyl group. The alkyl group can contain up to 3 hydroxy groups and/or the polyalkoxide chain can contain up to 30, preferably less than 10, alkoxide moieties.

Suitable alkyl polysaccharides are decyl, dodecyl, tetradecyl, pentadecyl, hexadecyl, and octadecyl, di-, tri-, tetra-, penta-, and hexagluco-sides, galactosides, lactosides, fructosides, fructosyls, lactosyls, glucosyls and/or galactosyls and mixtures thereof.

The alkyl monosaccharides are relatively less soluble in water than the higher alkyl polysaccharides. When used in admixture with alkyl polysaccharides, the alkyl monosaccharides are solubilized to some extent. The use of alkyl monosaccharides in admixture with alkyl polysaccharides is a preferred mode of carrying out the invention. Suitable mixtures include coconut alkyl, di-, tri-, tetra-, and pentagluco-sides and tallow alkyl tetra-, penta-, and hexagluco-sides.

The preferred alkyl polysaccharides are alkyl polyglucosides having the formula

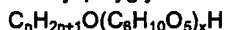


wherein Z is derived from glucose, R is a hydrophobic group selected from the group consisting of alkyl, alkylphenyl, hydroxyalkylphenyl, and mixtures thereof in which said alkyl groups contain from 10 to 18, preferably from 12 to 14 carbon atoms; n is 2 or 3 preferably 2, r is from 0 to 10, preferably 0; and x is from 1.5 to 8, preferably from 1.5 to 4, most preferably from 1.6 to 2.7. To prepare these compounds a long chain alcohol (R_2OH) can be reacted with glucose, in the presence of an acid catalyst to form the desired glucoside. Alternatively the alkyl polyglucosides can be prepared by a two step procedure in which a short chain alcohol (R_1OH) can be reacted with glucose, in the presence of an acid catalyst to form the desired glucoside. Alternatively the alkyl polyglucosides can be prepared by a two step procedure in which a short chain alcohol (C_{1-6}) is reacted with glucose or a polyglucoside ($x=2$ to 4) to yield a short chain alkyl glucoside ($x=1$ to 4) which can in turn be reacted with a longer chain alcohol (R_2OH) to displace the short chain alcohol and obtain the desired alkyl polyglucoside. If this two step procedure is used, the short chain alkylglucoside content of the final alkyl polyglucoside material should be less than 50%, preferably less than 10%, more preferably less than 5%, most preferably 0% of the alkyl polyglucoside.

The amount of unreacted alcohol (the free fatty alcohol content) in the desired alkyl polysaccharide surfactant is preferably less than 2%, more preferably less than 0.5% by weight of the total of the alkyl polysaccharide. For some uses it is desirable to have the alkyl monosaccharide content less than 10%.

The used herein, "alkyl polysaccharide surfactant" is intended to represent both the preferred glucose and galactose derived surfactants and the less preferred alkyl polysaccharide surfactants. Throughout this specification, "alkyl polyglucoside" is used to include alkyl polyglycosides because the stereochemistry of the saccharide moiety is changed during the preparation reaction.

An especially preferred APG glycoside surfactant is APG 625 glycoside manufactured by the Henkel Corporation of Ambler, PA. APG625 is a nonionic alkyl polyglycoside characterized by the formula:



wherein $n=10$ (2%); $n=12$ (65%); $n=14$ (21-28%); $n=16$ (4-8%) and $n=18$ (0.5%) and x (degree of polymerization) = 1.6. APG 625 has: a pH of 6 to 10 (10% of APG 625 in distilled water); a specific gravity at 25°C of 1.1 g/ml; a density at 25°C of 9.1 lbs/gallon; a calculated HLB of 12.1 and a Brookfield viscosity at 35°C, 21 spindle, 5-10 RPM of 3,000 to 7,000 cps.

The instant compositions can contain a silk derivatives as part of the composition and generally constitute 0.01 to 3.0 % by weight, preferably 0.1 to 3.0% by weight, most preferably 0.2 to 2.5% by weight of the liquid detergent composition.

Included among the silk derivatives are silk fibers and hydrolyzate of silk fibers. The silk fibers may be used in the form of powder in preparing the liquid detergent or as a powder of a product obtained by washing and treating the silk fibers with an acid. Preferably, silk fibers are used as a product obtained by hydrolysis with an acid, alkali or enzyme, as disclosed in Yoshiaki Abe et al., U.S. Patent No. 4,839,168; Taichi Watanabe et al., U.S. Patent No. 5,009,813; and Marvin E. Goldberg, U.S. Patent No. 5,069,898, each incorporated herein by reference.

Another silk derivative which may be employed in the composition of the present invention is protein obtained from degumming raw silk, as disclosed, for example, in Udo Hopp et al., U.S. Patent No. 4,839,165, incorporated herein by reference. The principal protein obtained from the raw silk is sericin which has an empirical formula of $C_{16}H_{25}O_3N_5$ and a molecular weight of 323.5.

Another example of a silk derivative for use in the liquid detergent composition of the present invention is

a fine powder of silk fibroin in nonfibrous or particulate form, as disclosed in Kiyoshi Otoi et al., U.S. Patent No. 4,233,212, incorporated herein by reference.

The fine powder is produced by dissolving a degummed silk material in at least one solvent selected from, for example, an aqueous cupriethylene diamine solution, an aqueous ammoniacal solution of cupric hydroxide, an aqueous alkaline solution of cupric hydroxide and glycerol, an aqueous lithium bromide solution, an aqueous solution of the chloride, nitrate or thiocyanate of calcium, magnesium or zinc and an aqueous sodium thiocyanate solution. The resulting fibroin solution is then dialyzed. The dialyzed aqueous silk fibroin solution, having a silk fibroin concentration of from 3 to 20% by weight, is subjected to at least one treatment for coagulating and precipitating the silk fibroin, such as, for example, by the addition of a coagulating salt, by aeration, by coagulation at the isoelectric point, by exposure to ultrasonic waves, by agitation at high shear rate and the like.

The resulting product is a silk fibroin gel which may be incorporated directly into the liquid detergent composition or the same may be dehydrated and dried into a powder and then dissolved in the liquid detergent composition.

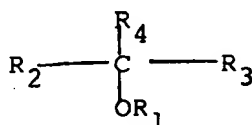
The silk material which may be used to form the silk fibroin includes cocoons, raw silk, waste cocoons, raw silk waste, silk fabric waste and the like. The silk material is degummed or freed from sericin by a conventional procedure such as, for example, by washing in warm water containing a surfact-active agent or an enzyme, and then dried. The degummed material is dissolved in the solvent and preheated to a temperature of from 60 to 95°C, preferably 70 to 85°C. Further details of the process of obtaining the silk fibroin are discussed in U.S. Patent No. 4,233,212.

A preferred silk derivative is a mixture of two or more individual amino acids which naturally occur in silk. The principal silk amino acids are glycine, alanine, serine and tyrosine.

A silk amino acid mixture resulting from the hydrolysis of silk of low molecular weight and having a specific gravity of at least 1 is produced by Croda, Inc. and sold under the trade name "CROSILK LIQUID" which typically has a solids content in the range of 27 to 31% by weight. Further details of the silk amino acid mixture can be found in Wendy W. Kim et al., U.S. Patent No. 4,906,460, incorporated herein by reference. A typical amino acid composition of "CROSILK LIQUID" is shown in the following Table.

AMINO ACID	PERCENT BY WEIGHT
Alanine	28.4
Glycine	34.7
Valine	2.0
Leucine	1.2
Proline	1.2
Tyrosine	0.6
Phenylalanine	0.9
Serine	15.4
Threonine	1.9
Arginine	1.5
Aspartic Acid	4.7
Glutamic Acid	4.1
Isoleucine	0.8
Lysine	1.4
Histidine	0.8
Cystine	0.1
Methionine	0.2
TOTAL	99.9

The instant compositions can contain a viscosity modifying solvent at a concentration of 0.1 to 5.0 weight percent, more preferably 0.5 to 4.0 weight percent. The viscosity modifying agent is an alcohol of the formula



wherein

$R_1 = CH_3, CH_2CH_3$

$R_2 = CH_3, CH_2CH_3$

$R_3 = CH_2OH, CH_2CH_2OH;$

$R_4 = H, CH_3$

which is preferably 3-methyl-3-methoxy-butanol.

The 3-methyl-3-methoxy butanol is commercially available from Sattva Chemical Company of Stamford, Connecticut and Kuraray Co., Ltd., Osaka, Japan.

The instant composition can contain 0.1 to 4.0% of a protein selected from the group consisting of hydrolyzed animal collagen protein obtained by an enzymatic hydrolysis, leucine protein, vegetal protein and hydrolyzed wheat protein and mixtures thereof.

The present light duty liquid detergents such as dishwashing liquids are readily made by simple mixing methods from readily available components which, on storage, do not adversely affect the entire composition. However, it is preferred that the nonionic surfactant be mixed with the solubilizing ingredients, e.g., ethanol and, if present, prior to the addition of the water to prevent possible gelation. The nonionic based surfactant system is prepared by sequentially adding with agitation the anionic surfactant and the betaine to the nonionic

surfactant, cosolubilizing agent and water, and then adding with agitation the formula amount of water to form an aqueous solution of the surfactant system. The use of mild heating (up to 100°C.) assists in the solubilization of the surfactants. The viscosities are adjustable by changing the total percentage of active ingredients. No polymeric or clay thickening agent is added. In all such cases the product made will be pourable from a relatively narrow mouth bottle (1.5 cm. diameter) or opening, and the viscosity of the detergent formulation will not be so low as to be like water. The viscosity of the detergent desirably will be at least 100 centipoises (cps) at room temperature, but may be up to 1,000 centipoises as measured with a Brookfield Viscometer using a number 3 spindle rotating at 18 rpms. Its viscosity may approximate those of commercially acceptable detergents now on the market. The detergent viscosity and the detergent itself remain stable on storage for lengthy periods of time, without color changes or settling out of any insoluble materials. The pH of this formation is substantially neutral to skin, e.g., 4.5 to 8 and preferably 5 to 5.5. The compositions of the instant invention are optically clear - that is they exhibit a light transmission of at least 95%, more preferably at least 98%.

These products have unexpectedly desirably properties. For example, the foam quality and deterative property is equal to or better than standard light duty liquid detergents while using a nonionic surfactant as the primary surfactant and minimal amounts of anionic surfactant, thereby achieving a mild, non-irritating liquid detergent.

The following examples are merely illustrative of the invention and are not to be construed as limiting thereof.

EXAMPLE 1

The following formulas were prepared at room temperature by simple liquid mixing procedures as previously described.

	A	B	C
NEODOL 1-9	15.5	12.5	14.5
Cocoamidopropyl Betaine	7	5.5	7
Na (AEOS.1.3 EO)	11.5	10.5	10.5
Sodium Bisulfite	0.05	0.05	0.03
Perfume	0.2	0.2	0.2
Water	Balance	Balance	Balance
Mono ethanol amide	0	1.5	--
MgSO ₄	3.1	3.1	3.5
HEDTA	0.08	0.08	0.08
Sodium Formate	2.0	2.0	2.0
Shell Foam	+	S	S
Shake-foam "Foam Height"	5	S	S
Brookfield viscosity LVTDV RT, #3 spindle, 18 rpms (cps)	410	350	428

The Shell Foam and Shake Foam Height test were run against a control sample of a commercial Palmolive Skin Sensitive formulation manufactured by Colgate-Palmolive Co. The designation "s" means that the sample being tested has the same value as the commercial sample. The designation "-" means that the value obtained is less than the value obtained for the commercial sample. The designation "+" means that the value obtained is superior to the value obtained for the commercial sample.

EXAMPLE 1

The following formula was prepared at room temperature by simple liquid mixing procedures as previously described

	A
Nonionic N odol 1-7	14.5
Elfan NS248 SMG (28% Al) AEOSE08:1 Magn sium Salt	17.86
Sodium lauryl sulfate (28%)	17
Cocoamido propyl betaine 30% Betadet HR-S(KAO)	16.67
Vencol (progiven)	1.5
EDTA	0.1
Sodium formate	2.0
Sodium bisulfite	0.05
Perfume	0.2
Water	Balance
Appearance	Clear
pH	5.0
Brookfield viscosity, RT #30 spindle, 10 rpm (cps)	600

Claims

1. A high foaming, light duty, liquid detergent comprising approximately, by weight,
 - (a) 10 % to 25 % of a water soluble nonionic surfactant selected from the group consisting of primary and secondary C₈-C₁₈ alkanol condensates with 5 to 30 moles of ethylene oxide, condensates of C₈-C₁₈ alkylphenol with 5 to 30 moles of ethylene oxide, condensates of C₈-C₂₀ alkanol with a heteric mixture of ethylene oxide and propylene oxide having a weight ratio of ethylene oxide to propylene oxide from 2.5:1 to 4:1 and a total alkylene oxide content of 60% to 85% by wieght and condensates of 2 to 30 moles of ethylene oxide with sorbitan mono and tri- C₁₀-C₂₀ alkanolic acid esters having an HLB of 8 to 15;
 - (b) 2 % to 12 % of a water-soluble betaine; and
 - (c) 8 to 16 % of an ethoxylated alkyl ester sulfate; and
 - (d) balance being water as an aqueous medium in which said nonionic surfactant, said ethoxylated alkyl ether sulfate and said betaine are solubilized in said water.
2. A liquid detergent composition according to Claim 1 further including 1.0 to 15% of a cosolubilizing agent selected from the group consisting of C₂-C₃ monoand di-hydroxy alkanols, water soluble salts of C₁-C₃, alkyl substituted benzene sulfonate hydrotropes and mixtures thereof.
3. A liquid detergent composition according to Claim 2 wherein ethanol is present in the amount of 5% by weight or less.
4. A liquid detergent composition according to Claim 2 wherein said nonionic surfactant is said condensate of a primary C₈-C₁₈ alkanol with 5-30 moles of ethylene oxide.
5. A liquid detergent composition, according to Claim 1 further including a perservative.
6. A liquid deterg nt composition according to Claim 1 further including a color stabiliz r.
7. A liquid d terg nt composition according to Claim 1 further including 0.5 to 8.0 wt. % f a cosolubilizing agent.
8. A high foaming, nonionic surfactant-bas d, light duty, liquid detergent comprising approximately, by

weight:

- (a) 10% to 20% of a water soluble nonionic surfactant selected from the group consisting of primary and secondary C_8 - C_{18} alkanol condensates with 5 to 30 moles of ethylene oxide, condensates of C_8 - C_{18} alkylphenol with about 5 to 30 moles of ethylene oxide, condensates of C_8 - C_{20} alkanol with a heteric mixture of ethylene oxide and propylene oxide having a weight ratio of ethylene oxide to propylene oxide from about 2.5:1 to 4:1 and a total alkylene oxide content of 60% to 85% by weight and condensates of about 2 to 30 moles of ethylene oxide with sorbitan mono and tri- C_{10} - C_{20} alkanolic acid esters having an HLB of 8 to 15;
 - (b) 8 to 16 % of a magnesium salt of an ethoxylated (C_8 - C_{18})alkyl ether sulfate surfactant;
 - (c) 0.5 to 8% of an alkali metal or ammonium salt of a C_8 - C_{14} alkyl sulfate surfactant;
 - (d) 2 to 10% of a water-soluble betaine surfactant; and
 - (e) balance being water as an aqueous medium in which said surfactants are solubilized in said water.
9. A liquid detergent composition according to claim 8 which includes, in addition, 1% to 15% by weight of a solubilizing agent which is a C_2 - C_3 mono or dihydroxy alkanols or a water soluble salts of C_1 - C_3 alkyl substituted benzene sulfonate hydrotropes and mixtures thereof.
 10. A liquid detergent composition according to claim 9 wherein ethanol is present in the amount of 5% by weight or less.
 11. A liquid detergent composition according to claim 9 wherein said nonionic surfactant is a condensate of a primary C_8 - C_{18} alkanol with about 5 to 30 moles of ethylene oxide.
 12. A liquid detergent composition according to Claim 8 further including a preservative.
 13. A liquid detergent composition according to Claim 8 further including a color stabilizer.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 94 40 1590

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP-A-0 387 063 (UNILEVER PLC) * page 2, line 44 - page 3, line 11 * * page 4, line 26 - page 5, line 15 * * page 5, line 22 - line 49 *	1-5,7-12	C11D1/94
Y	* page 6, line 14 - line 44 * ----	6,13	
X	US-A-3 950 417 (R.J.VERDICCHIO) * column 3, line 14 - line 30 * * column 3, line 31 - line 35 * * column 4, line 45 - line 61 * * column 5, line 59 - column 6, line 44 * ----	1,4-6	
X	DE-A-23 61 080 (THE PROCTER & GAMBLE CO.) * page 2, paragraph 4 - page 7, paragraph 4; example 1 * ----	1,4-6	
X	EP-A-0 155 737 (SHIONOGI&CO.) * page 2, line 21 - page 3, line 15 * * page 5, line 5 - page 7, line 7 * * page 7, line 17 - page 8, line 16 * ----	1,5	
X	EP-A-0 181 212 (THE PROCTER&GAMBLE CO.) * page 4, line 6 - page 6, line 23 * * page 13, line 13 - line 31; claims 1-7 * ----	1-5,7-11	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C11D
Y	WO-A-93 09215 (THE PROCTER & GAMBLE CO.) * claim 1 * -----	6,13	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 15 November 1994	Examiner Rotsaert, L
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document</p>			

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